REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*

2. REPORT TYPE
Technical Paper

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

5a. CONTRACT NUMBER
F04611-96-C-0005

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
1011

5e. TASK NUMBER
00KB

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Thiokol

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclassified	**Unclassified**	**Unclassified**	A		Leilani Richardson
					19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

1 item enclosed

1122 032

MEMORANDUM FOR PRS (Contractor Publication)

1 May 1998

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-1998-081**
L.F. Cannizzo et al. "Development of New Energetic Ingredients for Advanced Solid Rocket Propellants"
HEDM Conference **(Statement A)**

DEVELOPMENT OF NEW ENERGETIC MATERIALS FOR ADVANCED SOLID ROCKET PROPELLANTS*

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Abstract

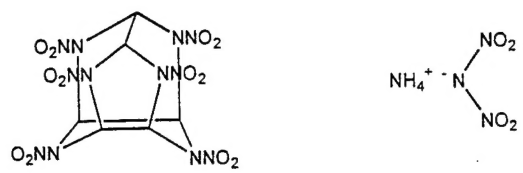
The Integrated High Performance Rocket Propulsion Technology (IHPRPT) Program has set ambitious goals of significant increases in rocket propulsion performance while maintaining acceptable cost and hazards criteria. As part of this effort, Thiokol Corporation has been actively investigating the synthesis, development, and formulation of new energetic ingredients for application in solid rocket propellants. Several new materials under investigation include CL-20 (a new high density nitramine), ADN (a high energy non-chlorine oxidizer), and heterocycle-based high nitrogen compounds. Recent propellant results indicate that attractive hazards properties and ballistic characteristics can be obtained with CL-20 and ADN.

Introduction

The IHPRPT Alternate Oxidizers and Fuels Program is directed towards achieving the Phase II and III propellant performance goals of the IHPRPT Program for booster and orbit transfer solid propellants.[1] The approach to meeting these goals is through the evaluation of alternate high energy oxidizers and fuels. These materials can be used to develop entirely new formulations and also to modify existing ones. Among the available alternate materials, the non-chlorine oxidizer ammonium dinitramide (ADN) can give dramatic increases in calculated Isp values compared to baseline ammonium perchlorate (AP) propellants. Utilizing technology developed on the Navy's ADN MANTECH Program, ADN of suitable quality for propellant formulating is now available. In combination with energetic binders, aluminized propellants containing ADN give formulations which can achieve the performance goals of the program. The recent, intensive effort to develop new energetic materials (e. g., CL-20, TNAZ) has lead to the availability of a number of high density, high heat of formation compounds which can be applied towards increasing solid propellant performance. The combination of these new materials with ADN and energetic binders now makes it possible to formulate solid propellants which can meet or exceed the predicted delivered performance of current metallized, AP-containing propellants in orbit transfer applications, without producing particulates or other products which might interfere with satellite systems.

Results and Discussion

The high density, energetic nitramine CL-20 was first synthesized in 1987 at the Naval Weapons Center, China Lake.[2] Thousands of pounds have been produced in the last several years by Thiokol Corporation using a modified process. Propellant grade material is now readily available for formulation studies. Utilization of low levels of CL-20 in both booster and orbit transfer formulations can give significant increases in solid propellant performance without causing unacceptable propellant safety properties. Recent propellant formulation efforts on the Air Force IHPRPT program with CL-20 have achieved both of these desired goals. The attractive ballistic characteristics of these propellants are shown in Figure 1. These include increasing burn rates and decreasing exponents as more CL-20 is incorporated into the propellant.



CL-20 **ADN**

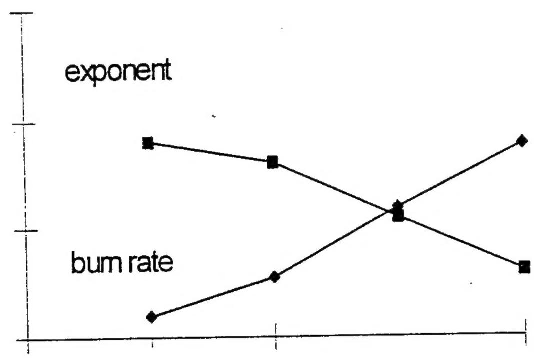


Figure 1. Ballistic Properties of High Energy CL-20 Propellants

Ammonium dinitramide (ADN) is currently under study by a number of researchers for various applications, including use as an oxidizer for solid rocket propellants.[3] The relatively good density and high heat of formation of this ingredient make it attractive for increasing the performance of booster and orbit transfer propellants. However, current properties of ADN which limit its use in solid propellants include poor thermal stability, deliquescence, and inferior particle morphology. The ADN MANTECH Program (sponsored by the Navy) has recently produced material which has significantly improved the above properties.[4] This has been accomplished by utilization of very low levels of additives combined with a prilling process to give spherical particles

of ADN. Using these techniques, multi-pound batches of prilled ADN have been manufactured for formulation studies. ADN-based propellants produced under the Air Force IHPRPT program have also shown attractive ballistics as has been found employing CL-20. A plot of some typical data is shown in Figure 2. Efforts are still underway to completely define the maximum level of ADN incorporation which still gives acceptable safety properties of the resulting propellants.

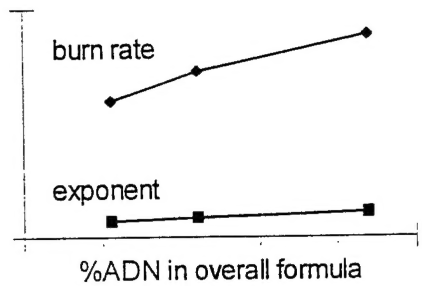
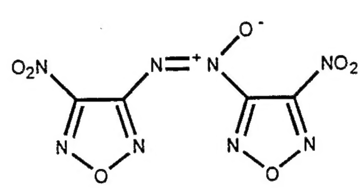


Figure 2. Ballistic Properties of High Energy ADN Propellants

Energetic compounds which contain nitrate ester and nitramine functional groups are inherently fairly sensitive to impact, friction and ESD stimuli due to the presence of these energetic moieties. However, other heteroatomic structures such as furazan, azoxy, azo and C-nitro groups can be used to construct energetic structures without the higher sensitivities noted above. Several such compounds are already known or in development.

Recent efforts have focused on improving the safety properties of DNAF such that scale up and formulation efforts can proceed. DNAF is synthesized in two steps from diaminofurazan. The intermediate compound diaminoazoxyfurazan (DAAOF) is obtained in 90% isolated yield.[5] Further oxidation of DAAOF with ammonium persulfate and hydrogen peroxide in concentrated sulfuric acid yields dinitroazoxyfurazan (DNAF) in 60% yield.[6] These literature procedures have been optimized at Thiokol to increase the yields and purities of the resulting products. Encouraging improvements in the safety properties of DNAF have been obtained when the remaining acid present from the synthesis is completely removed. This process requires that the DNAF be dissolved in a suitable solvent and then the resulting solution washed several times with aqueous sodium bicarbonate. The isolated material shows a significant improvement in friction sensitivity and thermal stability. However, smaller particle sizes of recrystallized DNAF are still sensitive to friction and ESD stimuli. The relevant data from these studies are presented in Table 1.



DNAF

Table 1. Safety Properties of DNAF*

properties	impact (inches)	friction (lbs)	ESD (joules)	DSC onset (°C)
baseline	15	13	>8	227
washed with bicarb	16	39	>8	247
washed with bicarb,	17	27	1.0	246

* Impact, friction, and ESD sensitivities were measured on Thiokol Corporation-designed instruments and are 50% levels. DSC onsets were determined at scan rates of 20°C/minute.

Another furazan-based compound, PIPER, is also under development. The current synthetic route under study is given in Figure 3. All but the last two steps have been optimized. The starting material for PIPER is DAF, the same material used to prepare DNAF. The penultimate step to form the precursor to PIPER has been performed on a several gram scale, but isolation of the product has proven difficult. Nitration of the precursor to yield PIPER has proven unsuccessful to date. Standard nitrating conditions either give unreacted starting material or decompose the precursor. Alternate conditions are currently being examined.

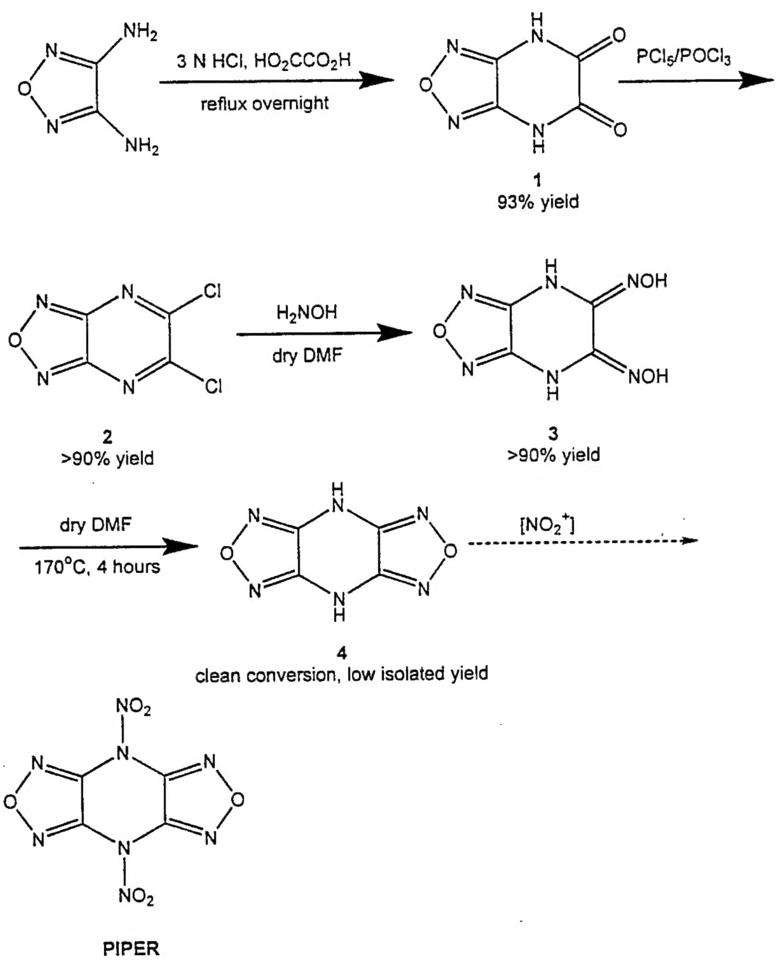


Figure 3. Current Route Under Development to Synthesize PIPER

Summary and Conclusions

As discussed in the previous pages, the utilization of new energetic oxidizers, fuels, and binders provides a viable approach to increasing the performance level of booster and orbit transfer propellants. The utilization of CL-20 in high energy booster propellants yields formulations with acceptable safety properties and attractive ballistics. ADN, when combined with energetic binder systems in aluminized propellants, give significant gains in predicted delivered performance compared to the baseline booster propellant. ADN propellants have also exhibited attractive ballistics. Work remains to find the maximum level of ADN incorporation which still gives acceptable safety properties. The furazan-based materials, PIPER and DNAF, are under development as potential high energy, low hazards propellant ingredients.

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